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# Conformational Transition in Poly(methyl methacrylate)

## 4. Influence of Solvent Nature

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## SUMMARY

This paper refers to a systematic and comparative study of the intrinsic viscosities of fractions of atactic and syndiotactic samples of PMMA in various polar solvents as a function of temperature. The data allow determination of important changes in the conformation of the polymer.

## INTRODUCTION

Viscometry, light scattering and differential refractometry give valuable information on the thermodynamic and conformational properties of macromolecules in solution. A study of atactic and synsiotactic samples of PMMA in polar and structurally analogous solvents has permitted us to determine, by application of theories of the excluded volume, the unperturbed dimensions, showing the existence of conformational change. The phenomena was also analyzed indicating their intervals and establishing the influence of the solvation power of the solvent.

## EXPERIMENTAL

The samples of syndiotactic PMMA were prepared by anionic polymerization (ROIG et al. 1971) using THF as solvent and biphenyl sodium as initiator (ROIG, FIGUERUELO 1966, ROIG et al. 1968). The polymer was precipitated with a methanol/water mixture (50 per cent v/v). The preparation of atactic PMMA samples has been previously described (KATIME et al. 1974; KATIME et al. 1975). All the samples were fractionated by solubility. By means of light scattering and membrane osmometry, the polydispersity of each sample under study was given by $M_w/M_n < 1.25$. The solvents (benzene, toluene, ethyl acetate, butyl acetate, methyl benzoate, acetone and cyclohexanone) were purified by standard procedures (TIMMERMANS, 1950).

Determination of intrinsic viscosity, $[\eta]$, was performed in a modified Ubbelohde viscometer. Measurements at high temperatures were made in a closed Ostwald viscometer. In all cases, kinetic energy corrections were made. The temperature range studied, for the atactic samples, was from 288 to 343 K and for the syndiotactic 263 to 343 K.

Weight-average molecular weight, $M_w$, were measured by light scattering in a FICA PGD model 4200 using green light (546

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nm). The photogoniodifusometer was previously calibrated with benzene using natural polarization and taking the Rayleigh ratio as $16.3.10^{-6}$ $cm^{-1}$(CARR, ZIMM, 1950). The refractive index increment, dn/dc, was measured in a Brice-Phoenix differential refractometer previously calibrated with solutions of highly purified KCl (Kruis 1936). Stereoregularity for each fraction was determined by NMR spectra in $CDCl_3$, according to Bovey and Tiers (BOVEY, TIERS 1960).

## RESULTS AND DISCUSSION

Plots of ln [η] versus temperature for two different fractions of syndiotactic and atactic PMMA in ethyl and butyl acetates, methyl and ethyl benzoates, acetone and cyclohexanone show anomalies as can be seen in Figure 1. In ethyl and butyl acetates, a decrease of [η] is seen between about 313 and 323 K, to increase again at higher temperatures. This effect can be due to conformational changes in the macromolecule (KATIME,VERA 1977a). Similar

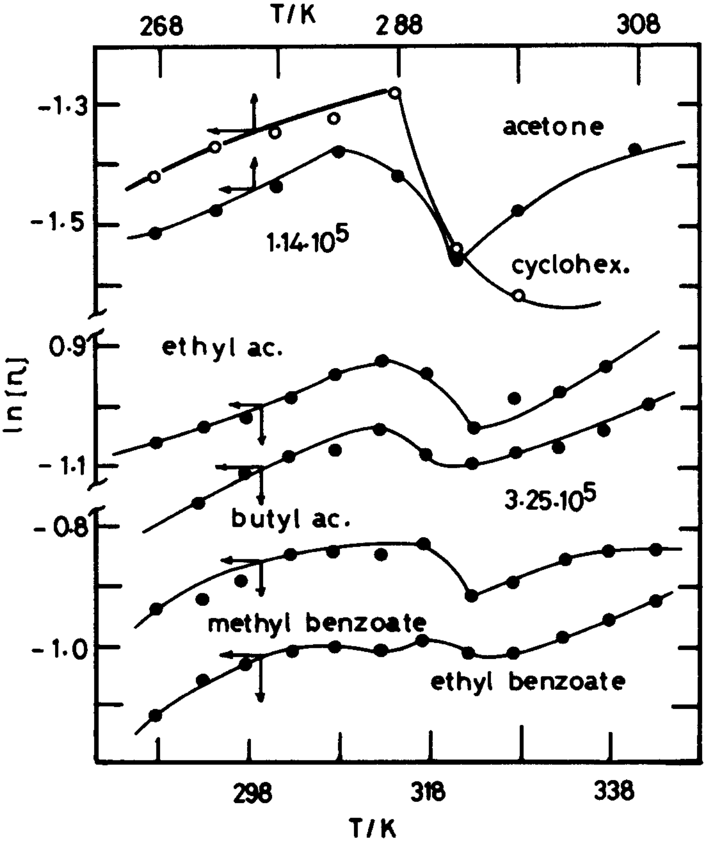

Figure 1. Variation with temperature of ln [η] for atactic PMMA($3.25.10^5$) in ethyl and methyl benzoate, ethyl and butyl acetate and syndiotactic PMMA($1.14.10^5$)in acetone and cyclohexanone

behaviour is shown by PMMA in methyl and ethyl benzoates (318-328 K). Analogous behaviour is found for syndiotactic PMMA in acetone (283-293 K) and in cyclohexanone (288-298 K). In general for low molecular weight samples, an inflexion in the ln $[\eta]$ versus temperature plot can be seen, indicating the temperature range where the conformational change takes place. If the molecular weight is high, the shape of the curve is not indicative of any transformation, because of the expansion of the chain that partially overlaps the phenomenon.

On the other hand, we can determine the unperturbed dimensions, $K_\theta$, by application of the Stockmayer-Fixman equation. We see that the $K_\theta$ values are not constant but vary sharply over the same temperature intervals previously observed in Figure 1.

If we define $\Delta K_\theta$ as the difference of the unperturbed dimensions before and after the conformational transitions, we find that its value for the aliphatic esters is $\sim$12% (Figure 2)

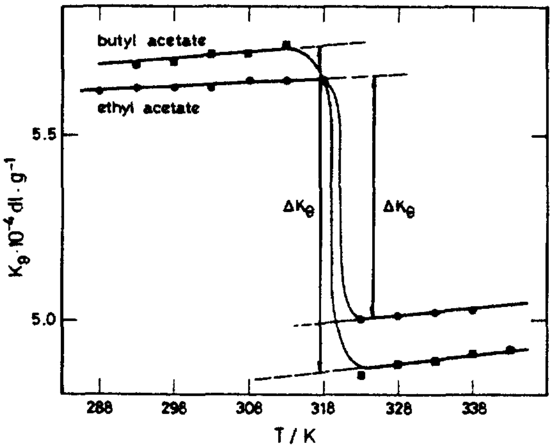

Figure 2. Variation of $K_\theta$ with temperature in methyl and butyl acetate for atactic PMMA.

and about 10% for the aromatic esters (Figure 3). These differences can be attributed to the different solvating powers, which are higher for the aromatic esters. Besides it has been observed that the $K_\theta$ values for the atactic samples in benzene and toluene are not the same as those for the aromatic and aliphatic esters (KATIME et al. 1977b). This may be due to a "solvent effect"(KURATA, STOCKMAYER 1963).

For syndiotactic PMMA in acetone and cyclohexanone, the observed $\Delta K_\theta$ is about 15% (Figure 4). However, it is important to observe that the interval of temperature where the transition is observed, $\Delta T_{trans}$, is not always the same. Thus, for atactic samples in the solvents studied, the conformational transition takes place between 313-323 K, while for syndiotactic PMMA it can be found between 283-298 K. We believe that the tacticity of PMMA is not necesarily the main factor involved in the different $\Delta T_{trans}$ and that the polarity of the solvent may be important.

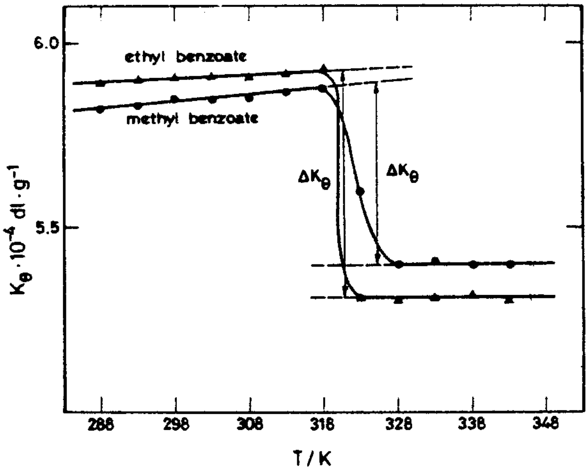

Figure 3. Variation of $K_\theta$ with temperature in methyl and ethyl benzoate for atactic PMMA.

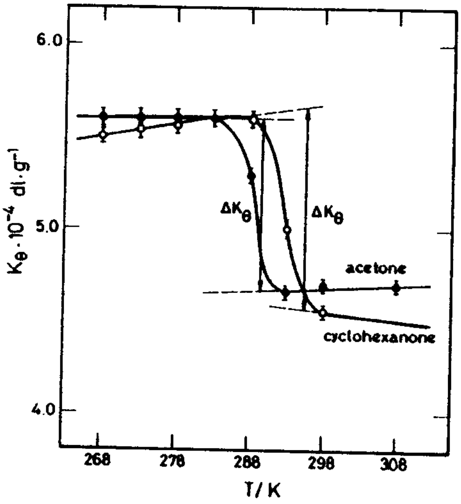

Figure 4. Variation of $K_\theta$ with temperature in acetone and cyclohexanone for syndiotactic PMMA.

Thus, for the conformational transition to occur, it is necessary for the macromolecule to reach an energy level such that the carbon atoms can mount the potential barrier and rotate around the valence cones. This energy state can be reach in various ways e.g. temperature increase or solvent interaction. In our case, we think that the observed difference are due to the fact that acetone as well cyclohexanone are considerably polar solvents, inducing a strong polymer-solvent interaction which supplies part of the energy so allowing a conformational change in PMMA at a lower temperature.

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